Physicochemical Properties of Green River Oil Shale, Particle Size
and Particle-Size Distribution of the Inorganic Constituents

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This paper presents information obtained regarding particle size and particle-size distribution of the inorganic constituents of Green River oil shale. Oil shale, a stratigraphic rock composed of a complex mixture of organic and inorganic constituents in variable proportions, is one of our major potential sources of liquid fuels. Pyrolysis is the basic principle common to the many experimental methods devised for converting the organic matter to liquid products. Many retorting systems have been developed, some to commercial or semicommercial scale (4,10,11). The similarity in percentage of organic matter converted to oil in such widely differing processes as a batch analytical method (13) and various large pilot plants operated at retorting temperatures of 850° to 950° F., indicates that the maximum conversion obtainable of organic matter to liquid products is of the order of 66 percent, regardless of the method of applying thermal energy. The other products formed are approximately 9 percent gas and 25 percent coke which remains on the shale residue. The published data further indicate that the crude oils produced are of poor quality (1,8,12). A definite explanation of these phenomena are not known. Probably they are a function of the molecular structure of the organic matter, the nature of the organic-inorganic association, the preferred reaction mechanism in a thermal system, or a combination of these factors.

As only 66 percent of the organic matter is converted to liquid products and the resulting oils are of poor quality, it would be highly desirable to develop processes that would improve both yield and quality of oil, thereby enhancing the economy of oil shale. Comprehensive understanding of the fundamental properties and structure of oil shale may improve existing methods or may disclose leads for devising new and better processes for converting the organic matter to liquid products. In the light of this, part of the research in oil shale is directed to gain a better insight into its physicochemical structure.

This is the first of a series of papers. Fundamental properties of oil shale currently under investigation are: Particle size and particle-size distribution of the primary inorganic particles; pore structure of the inorganic constituents; surface area of the raw oil shale and the inorganic constituents; pore size, pore-size distribution, and permeability of the inorganic matrix devoid of organic matter; and type of bonding between the organic and inorganic constituents. Information of this nature regarding oil shale is virtually nonexistent.

Experimental

Oil shales that differed widely in oil yield (75 and 28.6 gallons per ton) were selected for this investigation. Samples were taken at random from 1-foot-sections of beds EF and B, respectively, of the Selective mine, Rifle, Colo. (14). The 2 samples, approximately 200 pounds each, were crushed to pass a 2-mesh-per-inch screen.

Representative samples were taken and prepared as needed from each of the crushed samples.

Preliminary Considerations and Tests

Particulate materials usually respond favorably to particle-size measurements, but this is not the case with the primary inorganic particles that form part of the highly consolidated organic-inorganic system that exists in oil shale. The term "primary inorganic particles" is designated to mean the individual inorganic crystals. These crystals are either partly or entirely encased by organic matter and in many instances are bound together, in varying degrees, with inorganic cementing agents. The extent of the inorganic cementation is a function of the organic content. No practical or effective method is known whereby particle-size analyses of the primary inorganic particles can be made as they naturally occur in oil shale. It therefore became necessary to isolate the inorganic constituents. Removal of the organic matter by solvent action would have been ideal, as then the inorganic constituents recovered would have retained essentially their initial characteristics. However, no single solvent or combination of solvents was found that effectively separated the organic matter. Since solvent action did not accomplish the desired separation, the organic matter was removed by thermal treatment.

It was essential for comparative purposes that the organic matter be removed from the inorganic phase under a consistent set of conditions for all of the studies utilizing organic-free mineral constituents. In some studies the organic-free mineral constituents were prepared from many pieces of oil shale to form a single sample, whereas other studies required that organic-free mineral constituents be prepared from individual pieces of oil shale in the form of cores 1-1/2 inches long and 1/2 inch in diameter. The conditions selected for removing the organic matter, based on a series of preliminary tests, were those found that removed the organic matter from oil-shale cores with minimum physical and chemical changes to the mineral constituents.

Preparation of Organic-Free Mineral Constituents

Figure 1 presents a schematic diagram of the steps taken to prepare the organic-free mineral constituents. Two composites consisting of 200 to 300 pieces of oil shale ranging in size from 0.25 to 0.375 inch were selected from (1-B) to represent the 75-gallon-per-ton oil shale. The individual fragments were large enough so that any size reduction sustained by the primary inorganic particles exposed at the surfaces of the individual fragments during crushing of the oil shale were considered negligible. The composite samples were placed in separate porcelain dishes, arranged in the form of a bed 1-1/2 inches thick, covered, and placed in an electric muffle at room temperature. A thermocouple was placed in the center of one of the samples to record the bed temperature. The samples were heated to 250° F. over a period of one hour. The temperature of the oil-shale sample was raised in increments of 100° F. per hour to 650° F. It was maintained at 650° F. for six hours, then raised to 675° F. for an additional six hours and then to 700° F., until degradation of the organic matter appeared to be complete. This procedure was followed to permit the organic matter to escape from the individual pieces of oil shale with minimum structural breakdown of the inorganic matrix. Degradation of essentially all the organic matter appeared to occur between 650° and 700° F. At this phase of the thermal treatment the individual pieces were encrusted with carbonaceous material. The porcelain dishes were uncovered, and the temperature was maintained at 700° F. for four hours. During this period the carbonaceous material began to disappear slowly. The temperature was raised to 725° F. and maintained at this point for four hours. Any carbonaceous material remaining was removed at 750° F. Chemical analyses indicated that the shale residue obtained from this treatment contained less than 0.1 weight-percent of the initial organic carbon.

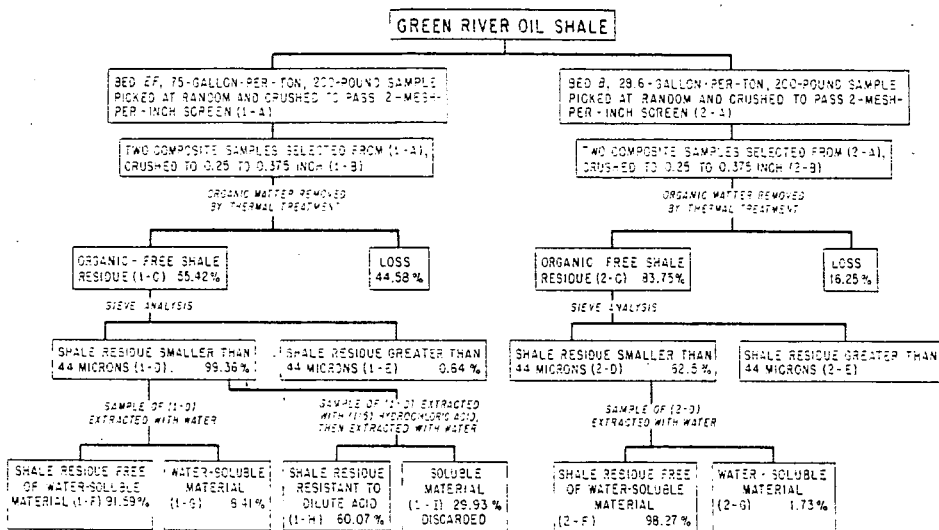Two composite samples of organic-free mineral constituents from 28.6-gallon-per-ton

FIGURE I.-SCHEMATIC DIAGRAM FOR PREPARING ORGANIC-FREE SHALE RESIDUE
FOR PARTICLE-SIZE MEASUREMENTS

oil shale (2-C) were prepared in the same manner as described above. Oil shale of this degree of richness was selected, as it occurs at several different levels in the Selective mine. The inorganic mineral constituents recovered from the 75- and 28.6-gallon-per-ton oil shales represented 55.42 and 83.75 weight-percent of the initial oil shale, respectively.

Mineral Constituents

The major inorganic constituents in the oil shales studied were quartz, feldspars, dolomite, and calcite, which compose approximately 95 weight-percent of the total mineral matter. The minor constituents include illite clay minerals, pyrite, and analcite. The constituents most sensitive to thermal treatment are the illite clay minerals, pyrite, and the carbonates. Grim (2) has shown by differential thermal curves that illite does not undergo formation of new phases at 750° F., or below. According to Jukkola et al., (5) the dolomite and calcite in oil shale do not decompose below 1000° F. Samples of organic-free shale residue maintained at 750° F. for eight hours had an average loss in weight of 0.15 weight-percent indicating that the shale residue did not undergo any appreciable loss in weight on prolonged heating.

Chemical Changes During Thermal Treatment

As a result of chemical changes that occurred during removal of the organic matter, the shale residue (1-C) contained 5.07 weight-percent calcium sulfate and 4.51 weight-percent ferric oxide. Formation of these compounds introduced particles foreign to the original inorganic constituents, as calcium sulfate and ferric oxide have been identified in only trace amounts in the minable bed. The ferric oxide most likely resulted from oxidation of the iron pyrite, and the calcium sulfate probably was formed by interaction between calcite and either organic or inorganic sulfur or a combination of both. Apparently the calcite was attacked instead of the dolomite in the formation of calcium sulfate, as no magnesium sulfate or free magnesium carbonate was detected in the shale residue. The calcium sulfate could be removed by prolonged continuous extraction with water. Because of density difference between the ferric oxide and the remainder of the shale residue, the conglomerated ferric oxide could probably be removed by gravity separation, using an appropriate liquid medium. However, effective separation by this method was not accomplished. Failure to separate the ferric oxide was attributed to physical forces interacting between the fine particles and liquid medium. Therefore the ferric oxide was included as part of the shale residue.

Particle-Size Measurements, Sieve Analysis

Particle-size measurements of the larger particles in the rich shale residue were determined by passing each of the two composite samples (1-C) over 30-, 60-, 80-, 100-, 200-, 300-, and 325-mesh sieves and weighing the primary inorganic particles retained on each sieve. Any shale residue that did not readily pass successive sieves was moved over the screen surfaces by applying pressure with a small brush. This method reduced conglomerated masses but was not severe enough to fracture primary particles. Hence, any new particles formed in reducing the conglomerates by this method were essentially fragments of cementing agents or possibly of some of the illite clay minerals. The combined weight of the primary particles retained on the sieves, above 600 and down to 44 microns in diameter, amounted to 0.64 weight-percent of the shale residue (1-C).

Particle-Size Measurements in the Subsieve Range

Microscopic examinations of the shale residue in the subsieve range (1-D) revealed that it still contained conglomerated masses. Reduction of these masses, except for some of the ferric oxide, was best attained by subjecting the shale residue suspended in a liquid medium to ultrasonic vibrations. The apparatus used to produce the

ultrasonic vibrations was a Glennite Model U-621 ultrasonic unit rated at 44 kilo-
cycles per second with a power output to the transducers of 100 watts. Primary parti-
cles of calcite and dolomite recovered on the 80- and 100-mesh sieves were exposed to
ultrasonic vibrations without significant deleterious effects. From these observations
it was concluded that the ultrasonic vibrations induced no appreciable shatter of the
primary particles.

Each composite sample of shale residue in the subsieve range (1-D) was divided
into three portions, as it was desired to obtain particle-size information of the
initial shale residue (1-D), the shale residue free of water-soluble material (1-F),
and that portion of the shale residue resistant to dilute hydrochloric acid (1-H).
The water-soluble-free and acid-resistant residues represented 91.59 and 60.07 weight-
percent of the initial shale residue (1-C). The respective specific gravities of the
three residues were 2.7443, 2.7354, and 2.6892. The continuous water extraction re-
moved 3.34 weight-percent of material other than calcium sulfate from the initial shale
residue (1-D).

Many different methods and apparatus, each with its merits and limitations, are
used for making particle-size measurements of materials in the subsieve range (6,15).
The method selected for this work was the increment method of sedimentation, considered
to be one of the most accurate methods; the apparatus was an Andreasen sedimentation
vessel. One limitation of this method is that particles with diameters smaller than
0.5 micron cannot be measured owing to Brownian movement, which prevents free fall.
Two important requirements for accurate particle-size measurements are a high degree of
dispersion of individual particles and subsequent prevention of flocculation during the
prolonged test period. These requirements were best attained when a suspension medium
was used that consisted of distilled water containing 2 grams per liter of Daxad No.
23 as the dispersing agent (7). Periodic examination of the suspension and the forma-
tion on standing of a rigid sediment of minimum volume indicated that the two require-
ments were attained to a high degree.

Duplicate determinations were made on each of samples (1-D), (1-F), and (1-H).
A weighed sample, sufficient to give an approximate volume concentration of 1 percent
of the volume of the sedimentation vessel, was mixed with 200 ml. of suspension medium;
and the suspension was subjected, with constant stirring, to ultrasonic vibrations for
30 minutes. The mixture was transferred to the sedimentation vessel, diluted to the
reference mark with suspension medium, and thoroughly mixed before it was placed in a
constant-temperature bath (70° F.) to minimize the effects of convection currents.
The suspension medium used to analyze (1-D) was saturated at 70° F. with calcium sulfate
to prevent any calcium sulfate in the shale residue from going into solution. After
temperature equilibrium was attained, the vessel was removed, thoroughly shaken for
several minutes, employing a tumbling motion, returned to the bath, and the first
10-ml. fraction immediately withdrawn and transferred to a tared beaker. Subsequent
fractions were withdrawn and transferred to tared beakers at increasing time intervals,
arbitrarily selected over a cumulative period of about 100 hours per analysis. Each
fraction except the first was withdrawn at uniform rate, approximately 20 seconds per
fraction, to minimize disturbance of the suspension. The number of fractions collected
totaled 20 to 22. After evaporation of the liquid and drying at 220° F., each fraction
was weighed and the correction applied for the dispersing agent. The corrected weight
of the first fraction represented the initial concentration of shale residue in the
suspension. The weight-percent of each subsequent fraction was calculated from the
initial concentration, and its corresponding particle size was determined by Stokes'
law, expressed as follows: (9)

$$r = \sqrt{\frac{9 h n}{2(d_1 - d_2) gt}},$$

where r is the radius of spherical particle (cm.); n, the viscosity of suspending medium (poises); h, distance (cm.) between liquid surface and pipette tip when sample is withdrawn; d_1, specific gravity of the particle; d_2, specific gravity of suspending medium; g, gravitational constant; and t, time in seconds. Stokes' law is based on the premise that particles are spherical and smooth and that the concentration of the suspension is dilute enough to permit free fall. Photomicrographs (Figures 2, 3, 4, and 5) revealed that the primary particles were essentially nonspherical. However, Lamar (7) states that irregular particles within the subsieve range have been shown to behave much like spheres. Hence, the results obtained by the sedimentation method should be valid.

The shale residue (2-C) from the 28.6-gallon-per-ton oil shale was subjected to a sieve analysis in the same manner described for the shale residue from the rich oil shale. The degree of cementation between individual primary particles was fairly extensive. As a result of this, only 62.5 weight-percent of the shale residue was reduced to within the subsieve range. Ultrasonic treatment did not effectively reduce the conglomerated masses retained on the sieves. To further reduce them would have required some form of crushing. Because of the high degree of cementation and low percentage (1.73) of water-soluble material (2-C), only the initial material in the subsieve range (2-D) was analyzed for particle size.

Interpretation of Results

Mathematical analysis of the direct analytical data from the sedimentation runs indicated that these data could best be expressed by converting them to a form that permitted graphic presentation, that is, cumulative weight-percent oversize as a function of the logarithm of equivalent spherical diameters. Figure 6 presents the cumulative size-distribution curve for the initial oil-shale residue (1-C). The linear plot represents the sieve analysis. If the primary particles had been spheres, the S-shaped curve would not show particles with diameters greater than 44 microns, as they would have been retained on the 325-mesh sieve. Overlapping of the two curves is attributed partly or entirely to the principle that sieves classify particles according to the least cross-sectional area. The material that remained in suspension after completion of the sedimentation run (7.20 weight-percent, with equivalent spherical diameters of less than 0.5 micron) was essentially calcium sulfate and illite clay minerals, as determined by X-ray diffraction. The total quantity of shale residue accounted for was 99.5 weight-percent of the shale residue analyzed.

Figure 7 presents the cumulative particle-size distribution curve of shale residue free of water-soluble material (1-F). The S-shaped curve represents the average particle size based on the analytical data from two composite samples. The degree of conformity between the two samples, as exhibited by the plotted points, was such that only one curve could be conveniently presented. The linear plot represents the sieve analysis. The total quantity of shale residue accounted for represented 98.8 weight-percent of the shale residue analyzed, of which 3.2 weight-percent remained in suspension. The material that remained in suspension was essentially illite clay minerals.

The cumulative particle-size distribution curve for the shale residue treated with dilute hydrochloric acid (1-H) is shown in Figure 8. The major constituents in the acid-resistant residue were quartz and feldspars. The S-shaped curve represents the average of two sets of experimental data taken from two composite samples of shale residue. The plotted points show the actual values calculated from the analytical data. The quantity of shale residue with equivalent spherical diameters less than 0.5 micron that remained in the suspension medium at the end of the run was 2.6 weight-percent. The total quantity of shale residue accounted for was 98.5 weight-percent of the shale residue charged to the sedimentation vessel.

Figure 9 presents the cumulative particle-size-distribution curve for the primary
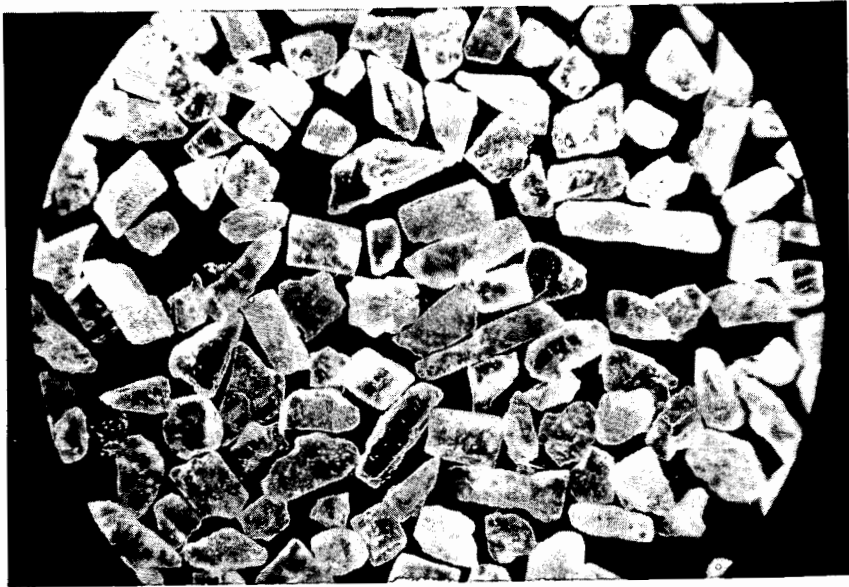
Figure 2. Photomicrograph of primary inorganic particles illustrating shape and roundness. Equivalent spherical diameter range, 175 to 250 microns. Magnification 30X.
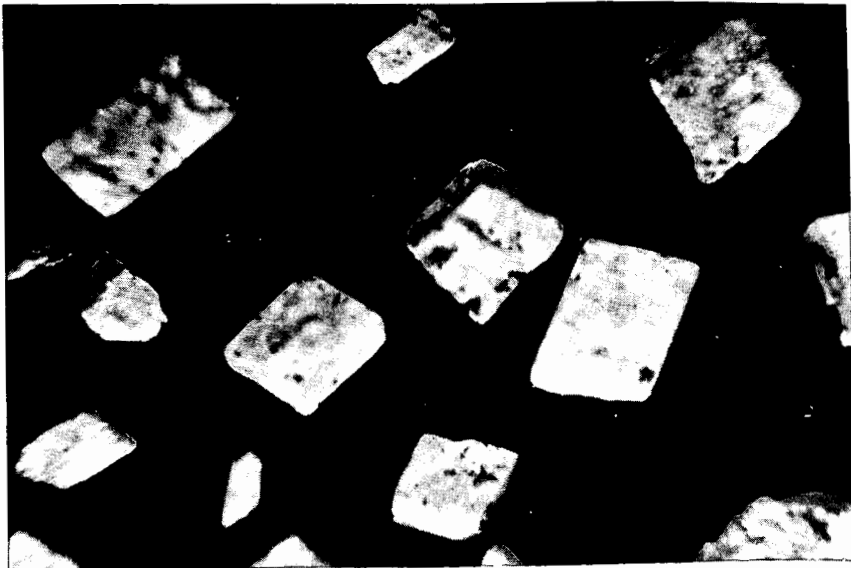

Figure 3. Photomicrograph of primary inorganic particles shown above. Magnification 100X.
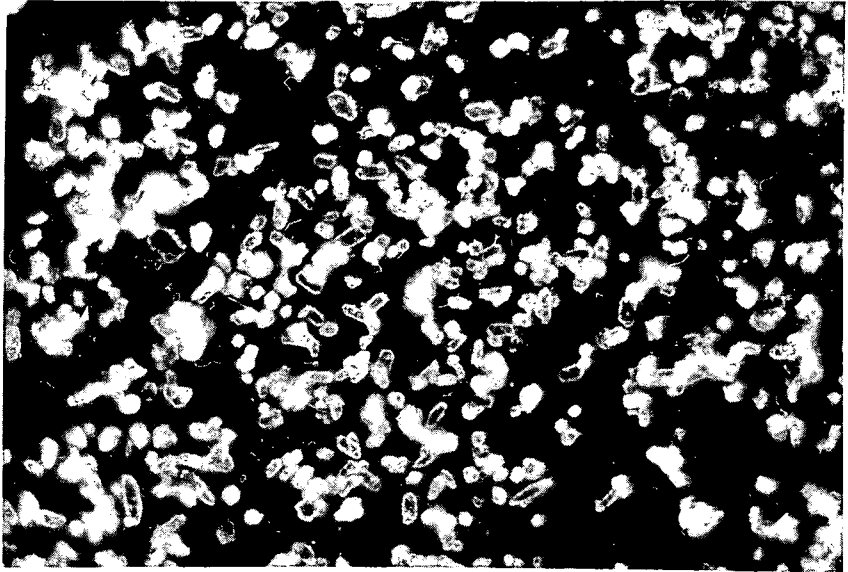
Figure 4. Photomicrograph of primary inorganic particles. Equivalent spherical diameter range, 5 to 15 microns. Magnification 210X.
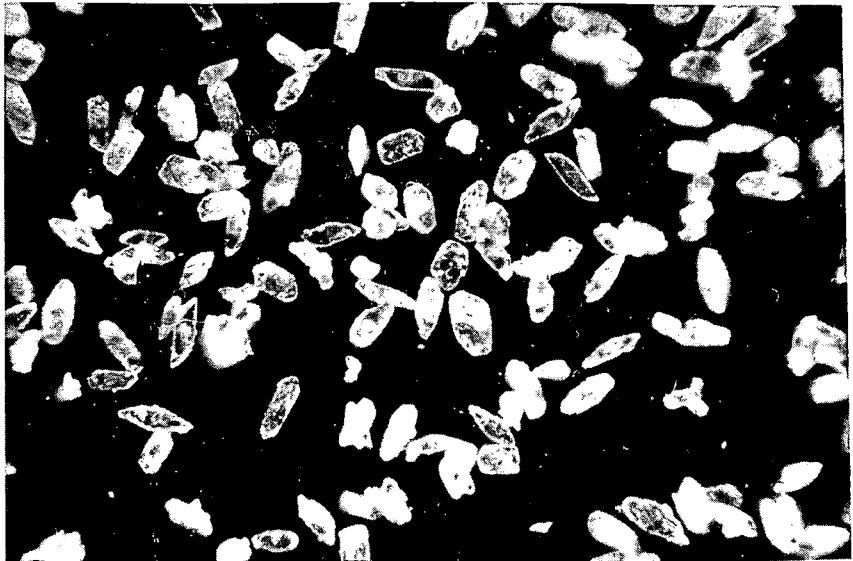

Figure 5. Photomicrograph of primary inorganic particles, essentially quartz and feldspars. Equivalent spherical diameter range, 15 to 30 microns. Magnification 210X.
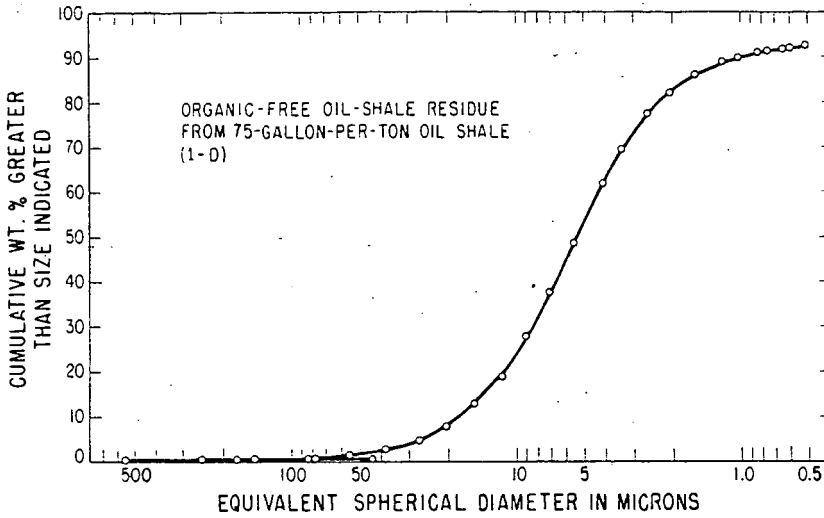
FIGURE 6.-CUMULATIVE PARTICLE-SIZE DISTRIBUTION CURVE OF THE
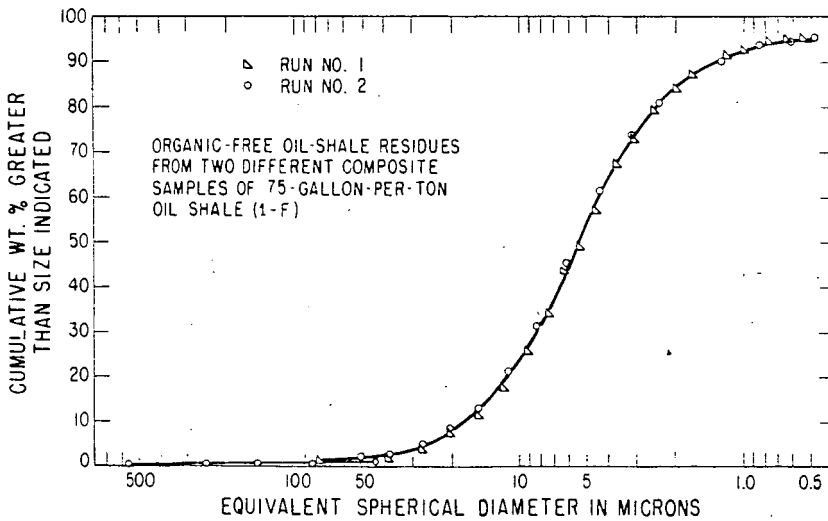PRIMARY INORGANIC PARTICLES IN RICH OIL SHALE

FIGURE 7.-CUMULATIVE PARTICLE-SIZE DISTRIBUTION CURVE OF PRIMARY
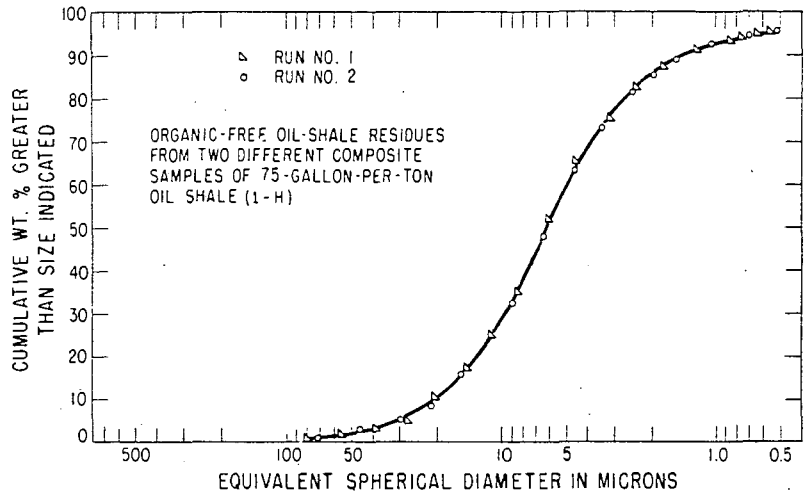INORGANIC PARTICLES FREE OF WATER-SOLUBLE MATERIAL

FIGURE 8.-CUMULATIVE PARTICLE-SIZE DISTRIBUTION CURVE OF PRIMARY
INORGANIC PARTICLES FREE OF WATER-SOLUBLE AND DILUTE
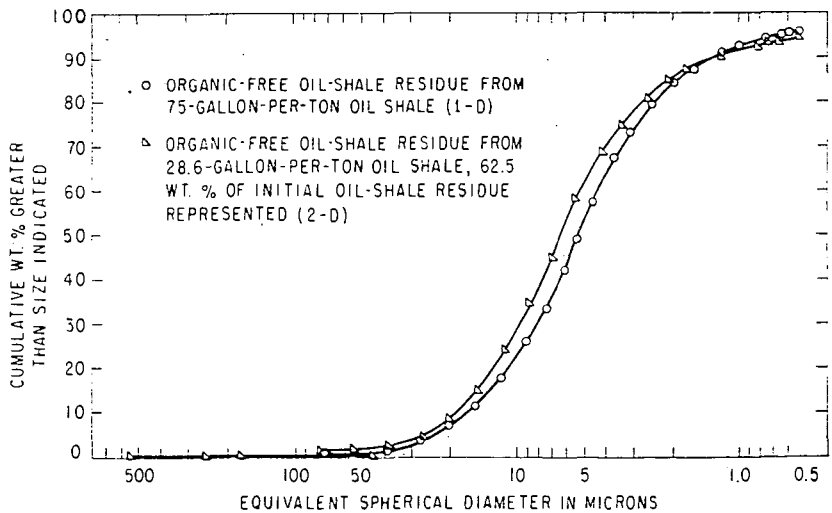MINERAL ACID-SOLUBLE MATERIALS

FIGURE 9.-CUMULATIVE PARTICLE-SIZE DISTRIBUTION CURVES OF
PRIMARY INORGANIC PARTICLES IN 75-AND 28.6-GALLON-
PER-TON OIL SHALE

inorganic particles (2-D), 28.6-gallon-per-ton oil shale, that passed through the 325-mesh sieve. The plot of Figure 6 is included in Figure 9 for the purpose of comparing particle size and particle-size distribution of primary inorganic particles in oil shale taken at two different levels within the oil-shale formation. The oil shales from these two levels differed widely in organic content. It is noted that both size and distribution of the primary particles within the two levels exhibit a high degree of similarity. Microscopic examination of the portion of the shale residue that did not reduce to primary particles (2-E) during the screen analysis indicated that the sizes of the primary particles constituting the conglomerated masses were of the order of those that passed the 325-mesh sieve.

The direct results of all the sedimentation analyses in the form of cumulative weight-percent oversize as a function of equivalent spherical diameters in microns plotted as S-shaped curves. The plots indicate that distribution of sizes of the primary inorganic particles in Green River oil shale tends to follow a log-normal distribution. Good agreement to log-normal distribution was noted between equivalent spherical diameters ranging from approximately 1.7 to 35 microns when these data were plotted on logarithmic probability paper. Departure from log-normal distribution was noted above and below these diameters. Cumulative frequency curves that are log-normal plot as linear lines on logarithmic probability paper. Information available from the cumulative frequency curves are, particle-size range of the primary inorganic particles, weight-percent of shale residue above or below a given diameter, or weight-percent of shale residue within any two size ranges except for the shale residue smaller than 0.5 micron. Two parameters that normally define distribution curves of this type (geometric mean size and standard geometric deviation) may be calculated from the S-shaped curves by reading appropriate intercepts. The geometric mean size is the value in microns corresponding to 50-weight-percent oversize, and the standard geometric deviation is the ratio of sizes corresponding either to 84.13 and 50.00 or 50.00 and 15.87 weight-percent oversize (3). The geometric mean sizes of the primary inorganic particles determined from the distribution curves of shale residues represented by (1-D), (1-F), (1-H), and (2-D) were 5.3, 5.4, 6.2 and 6.4 microns, respectively. The values of the standard geometric deviations for the above curves, as calculated from the ratio of sizes corresponding to 84.13 and 50.00 percent oversize, were 0.3, 0.4, 0.4, and 0.3, respectively. Calculated from the ratio of sizes corresponding to 50.00 and 15.87, the values obtained for the standard geometric deviation were 0.4.

Geometric Form of Primary Inorganic Particles

Information concerning two fundamental properties of the primary inorganic particles -- shape and roundness -- is best conveyed with photomicrographs. Figure 2 illustrates primary inorganic particles retained on a minus 60-plus 80-mesh sieve. The particles are predominantly rhombic. Increased magnification of a number of these particles brings out the third dimension and some of their surface characteristics, as noted in Figure 3. Figure 4 illustrates primary particles with equivalent spherical diameters ranging from 5 to 15 microns. The geometric configuration of the primary particles, with equivalent spherical diameters smaller than 5 microns, could not be brought out clearly with photomicrographs. However, microscopic examination of these particles revealed that their geometric form resembled that shown in Figure 4. Figure 5 illustrates the primary particles that were resistant to dilute hydrochloric acid. The equivalent spherical diameter of these particles, essentially quartz and feldspars, ranged from 15 to 30 microns. X-ray analyses indicated that the sharp-pointed particles were quartz.

Summary

The results of this investigation provide better understanding of the particle

size, particle-size distribution, and geometric form of the primary inorganic particles present in Green River oil shale. Because particle-size studies could not be made in the presence of the organic matter, it was removed by thermal treatment in a manner that minimized chemical and physical changes to the mineral constituents. By virtue of its high organic content, oil shale that assayed 75 gallons per ton yielded a friable residue amenable to this type of work. The portion of shale residue from the 28.6-gallon-per-ton oil shale that reduced to primary inorganic particles without crushing — 62.5 weight-percent — was used for particle-size studies.

The primary inorganic particles were essentially nonspherical, and their predominate geometric form appeared to be rhombic. More than 99 weight-percent of the primary inorganic particles analyzed had equivalent spherical diameters less than 44 microns. The distribution of sizes tend to follow a log-normal distribution between equivalent spherical diameters ranging from 1.7 to 35 microns. Departure from log-normal occurred below and above these values. The geometric mean size and standard geometric deviation of the primary inorganic particles free of water-soluble material in the 75-gallon-per-ton oil shale were 5.4 microns and 0.4, respectively. The corresponding values for that portion of the 28.6-gallon-per-ton oil shale residue analyzed were 6.4 microns and 0.3. The range of sizes and type of distribution of the primary inorganic particles of oil shales that differed widely in organic content and represented two different levels within the Green River formation appeared to be quite similar.

Acknowledgment

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